



The integration of ozonation catalyzed with MgO nanocrystals and the biodegradation for the removal of phenol from saline wastewater

Gholamreza Moussavi*, Ali khavanin, Rahimeh Alizadeh

Department of Environmental & Occupational Health, Faculty of Medical Sciences, Tarbiat Modares University, Ale Ahmad Highway, Tehran, Iran

ARTICLE INFO

Article history:

Received 31 January 2010

Received in revised form 24 March 2010

Accepted 27 March 2010

Available online 2 April 2010

Keywords:

Saline wastewater

Phenol

Advanced oxidation process

Catalytic ozonation

Biological process

ABSTRACT

Efficient treatment of saline wastewaters, particularly those containing inhibitory and toxic compounds, has been a challenge in recent years. This study proposed and investigated an efficient option for treating such streams. An MgO nanocrystal mesoporous powder was prepared from natural magnesite, and its potential to serve as a catalyst for degradation and chemical oxygen demand (COD) removal of phenol from saline wastewater was evaluated. The influence of several parameters including pH, dose of MgO nanocrystals, and NaCl concentration was investigated on the catalytic ozonation process (COP) of phenol in saline wastewater. The concentration of NaCl had no adverse influences on the phenol degradation. The results indicated that 96% of the phenol and 70% of the COD were removed in the COP (initial phenol concentration was 1100 mg/L and initial COD was 2500 mg/L) under optimum experimental conditions of pH 7 and a 4 g/L catalyst dose after an 80 min reaction time. A synergistic influence of about 39% was observed for phenol degradation in the COP. The effluent from the COP obtained from the aforementioned conditions was efficiently post-treated in a batch biological reactor, such that after 10 h of aeration, the COD was reduced to around 20 mg/L. In contrast, it took 50 h for reduction of COD to below 100 mg/L when adding raw phenol wastewater into the bioreactor. Therefore, the prepared powder was found to be an efficient and promising catalyst for ozonation, and coupling the developed COP with a biological process might be an attractive treatment option for saline wastewaters containing high concentrations of toxic compounds.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

As a result of the increasing number of industries throughout the world, the generation of industrial effluents having different contaminants is thereby increasing, which has become a main concern from the viewpoints of sustainable development and environmental protection. One of the most ubiquitous industrial wastewater contaminants is phenol [1], which is present in high levels in the effluent from numerous industries including chemical, petrochemical, pharmaceutical, refineries, oil field activities, coal processing, olive oil production, etc. [1–3]. Phenol is toxic to humans and causes headaches, fainting, vertigo and mental disturbances. Additionally, it can cause several severe ecological and environmental problems in receiving environments [4]. Wastewater generated in many of the above-mentioned industries commonly contains high concentrations of phenol and dissolved solids in particular chloride salts [5,6], which render its handling very difficult. Indeed, salts in high concentrations can inhibit the performance of biological processes [7,8].

Several physical, chemical and biological methods or combinations thereof are available for removing the organic compounds, such as phenolic compounds, from the wastewaters. Biological processes are commonly adopted as the first option for treating wastewater containing biodegradable contaminants due to their efficacy, cost-effectiveness, operation simplicity and environmental compatibility advantages; however, they are not appropriate techniques for removing biorecalcitrant compounds [2]. The phenolic compounds are known to be refractory and resistant to biodegradation and are thus biorecalcitrant due to their aromatic structure [9–11]. Therefore, they can inhibit the biodegradation reaction at concentrations above 50 mg/L [12].

Physical methods are only phase-changing unit operations that simply transfer the contaminants into another phase like that attained in adsorption, and they still elicit environmental concerns. Therefore, using chemical processes in particular as a pretreatment option for partial oxidation of resistant organics and converting those products into simple and biodegradable intermediates are highly necessary [13,14] and have recently been the subject of significant attention.

Due to their high capability in destroying organic compounds, the advanced oxidation processes (AOPs) are among the chemical processes most attractive for treating wastewater containing

* Corresponding author. Tel.: +98 21 82883827; fax: +98 21 82883825.

E-mail address: Moussavi@modares.ac.ir (G. Moussavi).

inhibitory and toxic contaminants [15]. The main feature of an AOP is the generation of very reactive radicals [15], mainly $\cdot\text{OH}$, at ambient temperature and pressure, which non-selectively degrades the organic molecules they come into contact with [16,17]. COPs are the recently emerged and attractive types of AOPs in which a material such as a homogenous or heterogeneous catalyst is accompanied with the ozone to generate highly powerful oxidative radicals [18,19]. Heterogeneous COP has recently attained much attention as the most attractive and preferred option due to its ease of catalyst retrieval [20], higher degradation efficiency [21], simplicity of operation, non-residual catalyst in the treated wastewater [22,23] and lower cost [24].

Although several works have been published so far on using COP for the degradation of different contaminants, investigation of this process in terms of removal of contaminants from saline media is very rare. Furthermore, although the catalytic capabilities of several materials including activated carbon, metal ions and oxides, natural zeolites and ores, and impregnated materials have been studied in COPs [20], finding an active and stable material for use as a catalyst to achieve an optimized COP for oxidation of organic contaminants in liquid streams has remained a challenge [25]. In this regard, the research on COPs in recent years has been focused on the synthesis and study of nano-sized metal oxides as catalysts [e.g., 24,26–29], and it seems that efficient and suitable alternatives are continuing to be found.

We have recently shown that MgO nanocrystals are efficient catalysts in the catalytic ozonation of dye [22] and formaldehyde [30]. In effect, MgO contains surface basic sites [31], and it has a destructive adsorbance [32], high surface reactivity, high adsorption capacity, high specific surface area [33], and it is hard and almost non-soluble in water. Moreover, if leached into the liquid under treatment, magnesium is not toxic and would not cause water pollution. These properties present MgO as a very suitable and deserving candidate for use in the catalytic ozonation context, particularly in saline media where the radical scavenging species interfere with the oxidation reaction and compete with the target compounds in utilizing the oxidative radicals [34–36]. Although MgO has been previously used as a catalyst in the catalytic ozonation of phenol [37] and dyes [22] giving a high catalytic activity, no report could be found either on the preparation of nanocrystal MgO from natural magnesite or on catalytic ozonation of the saline wastewaters.

Despite their high degradation efficiencies, the intermediates produced during organic degradation in an AOP are generally smaller and thus more difficult to mineralize, and they are generally more biodegradable than the original molecules [38]. Hence, using AOPs for complete mineralization of the toxic organics requires extensive operating conditions [39]; consequently, cost is generally expensive, and it is not affordable to use AOPs as the stand-alone treatment process for mineralization of organic compounds [40]. Hence, there is a great advantageous potential of coupling an AOP with a biological process to attain a more efficient and cost-effective technology for treating low biodegradable or toxic compounds [20,41,42].

Based on the above introduction, combining COP with the biological process for phenol removal in saline wastewater provides a possibility for overcoming the inhibitory influences of phenol to microorganisms' activity through its partial degradation in COP into simple and low molecular organic acids [42], which would be easily mineralized in a subsequent biological process. Accordingly, the evaluation of the performance of MgO nanocrystal-based COP for phenol degradation in saline wastewater is required to find its optimum operational conditions and capability in treating such difficult-to-treat streams. Also, an investigation to determine the effectiveness of the biological post-treatment process as a post-treatment option in the removal of intermediates generated in the

COP stage of phenol oxidation in saline wastewater is still required. The availability of huge mines of very high-quality magnesite in Iran provides a low-cost and natural-based mineral material for preparation of nanocrystal MgO for application in COPs.

The novelty of the present investigation is as follows: (1) the preparation of MgO nanocrystal powder from the natural mineral of magnesite, (2) the comparison of the prepared MgO nanocrystals to the raw magnesite in their use as catalysts for catalytic ozonation of phenol in saline wastewater, and (3) the evaluation of the integrated nano-MgO-based COP/biological process for degradation and COD removal of phenol in saline wastewater. In COP experiments, the influence of several important factors such as solution pH, concentration of NaCl, and catalyst dose on phenol degradation in saline wastewater was tested. The mechanism of phenol degradation was also investigated. For the post-treatment phase, the effluent from catalytic ozonation experiments under the optimum experimental conditions was treated in a batch biological process with suspended biomass.

2. Materials and methods

2.1. Preparation of catalyst

MgO nanocrystal powder was prepared from natural mineral magnesite obtained from West Azerbaijan, Iran. The natural magnesite ore was first crushed into fine particles, washed with distilled water, and then dried. The MgO was made using the calcination method [43]. For preparation of the catalyst, the natural magnesite particles were first grinded and then washed with distilled water (soaked in acid for 2 h) to remove the surface impurities. The water was then poured out, and the powder was allowed to dry at 100 °C in a dryer for 24 h. The dried powder was then calcined in a furnace at 700 °C for 2 h. Finally, the prepared catalyst was manually powdered in a mortar, and this powder was characterized and used in the COP as a catalyst.

2.2. Catalytic ozonation experiments

The catalytic potential of the prepared MgO nanocrystals was assessed by degradation of phenol in saline media using COP, compared with single ozonation and catalytic ozonation with natural magnesite powder. The experiments were carried out in a batch cylindrical glass reactor as detailed elsewhere [19]. The influences of several parameters including solution pH, NaCl concentration, dose of catalyst, and the reaction time were investigated on the phenol degradation using catalytic ozonation with the prepared MgO nanocrystals. The ozonation rate was constant at 0.25 g/h throughout the experiment. The phases of experiments along with the experimental conditions are given in Table 1. For each test, 200 mL of 1100 mg/L phenol solution prepared in distilled water were poured into the reactor. The desired conditions (Table 1) were regulated, and the solution was ozonated for the given time. The contents in the reactor were then centrifuged at 10,000 × g for 10 min, and the clear solution was analyzed for residual phenol and chemical oxygen demand (COD) to determine the efficacy of the COP. The phenol degradation degree in COP under optimum conditions was calculated from the total COD of the solution before and after the reaction.

2.3. Biological post-treatment experiments

After evaluating the catalytic ozonation of phenol in saline wastewater, the conditions at which the phenol concentration was decreased to below 100 mg/L were selected as optimum conditions for heterogeneous catalytic ozonation of phenol in saline wastewater using the prepared MgO nanocrystals. This level of

Table 1
Phases and conditions of the experiment.

Phase	Aim	Catalytic ozonation experimental conditions ^a					Biological post-treatment
	Type of catalyst	pH	NaCl (g/L)	Dose of catalyst (g/L)	Solution temperature (°C)	Reaction time (min)	
1	Investigation of the efficiency of the catalysts	• Natural magnesite • Prepared catalyst (MgO)	7	20	5	25	5–80
2	Influence of solution pH	MgO	5–10	20	5	25	–
3	Influence of solution salinity	MgO	7	0–50	5	25	–
4	Influence of catalyst dosage	MgO	7	40	0 (SOP) ^b	25	–
5	Degradation mechanism and kinetic, and COD removal	MgO	7	40	4	25	–
6	Biological post-treatment of COP effluent	MgO	7	40	4	25	80

^a The concentration of phenol was considered constant at 1100 mg/L throughout of the study.

^b SOP: single ozonation process. A test without ozonation was also conducted with 5 g/L catalyst to determine the adsorption of phenol onto the catalyst.

organic compounds is usually acceptable for biological treatment processes. Therefore, the effluent of the COP from the optimum conditions was further treated in a suspended biological batch reactor. The bioreactor consisted of a 0.3-L glass column equipped with a diffuser to distribute the air into the microbial suspension. The degradation and COD removal of the remaining phenol in the COP effluent were tested in a batch bioreactor over several aeration times between one and 10 h. To highlight the influence of COP pretreatment in removal of phenol from saline wastewater, the treatment of raw saline wastewater containing phenol (without pretreatment) was also studied in the same bioreactor. The mixed liquor from a bench-scale bioreactor treating saline wastewater containing phenol was used as a seed in the biological post-treatment tests. For the biological tests, 30 mL of concentrated biomass was mixed with 170 mL of wastewater (raw or pre-treated) in the bioreactor, giving a biomass concentration of 2000 mg/L (measured as volatile suspended solids), and then the suspension was aerated for a certain time. After the specified aeration time, the suspension was allowed to settle for 1 h, and it was then filtered with 0.45-μm Whatman filter paper. The filtrate was then analyzed for remained phenol and COD.

2.4. Catalyst characterization and analytical methods

The compositions of the natural magnesite mineral and the prepared powder were determined using the X-ray fractionation technique. The prepared powder was characterized by determination of crystallite, specific surface area, volume of pores, surface morphology, and size of the formed crystals. The N₂ adsorption/desorption method was used at 77 K (Micromeritics/Gemini-2372) to measure the BET specific surface area and pore volume of the prepared catalyst. From this data, the average pore size was calculated according to the equation reported by Altenor et al. [44]. Surface morphology of the prepared powder was observed by scanning electron microscopy (SEM) using a Philips-XL30 Electron Microscope. The crystalline phases of the fabricated catalyst particles were evaluated based on the X-ray diffraction technique (Philips-XPERT) using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$), scanned for 2θ between 20 and 80°. The size of the crystals was calculated from the Scherrer equation [45].

The concentrations of phenol were measured based on the colorimetric method by measuring the maximum absorption wavelength at 500 nm with the Unico-UV 2100 UV-vis spectrophotometer. COD was determined according to the procedure detailed in the standard method, with adding high amount of HgSO₄ for overcoming the interference of chloride ions. The intermediates formed during the degradation of phenol in COP experiments were not specified; however, they were grossly quantified by subtraction of the total COD and the phenol equivalent COD in the centrifuged samples at the end of the target reaction tests [46]. The concentration of ozone in the inlet gas stream was measured using its absorption in the 2% KI solution with subsequent titration against a standard sodium thiosulfate titrant [47]. pH was analyzed by the corresponding calibrated pH-electrode. Temperature was measured using a mercury thermometer.

3. Results and discussion

3.1. Catalytic ozonation process

The first phase of the experiment was the preparation of a natural mineral-based catalyst from magnesite and the investigation of its catalytic potential in enhancement of the ozonation process for

Table 2

Composition of the natural and calcined magnesite.

Composition	Material (wt.%)	
	Natural magnesite	Calcined magnesite
MgO	50.45	95.02
SiO ₂	0.45	0.346
CaO	0.218	0.381
Al ₂ O ₃	0.077	0.076
Fe ₂ O ₃	0.073	0.107
LOI ^a	48.71	3.785
Others	<0.02	<0.3
Total	100	100

^a LOI: loss of the ignition.

degradation of phenol in saline wastewater. The results from this phase of the study are presented and discussed below.

3.1.1. Characteristics of the prepared catalyst

The chemical composition of the prepared catalyst, determined using the XRF technique at the beginning of the study, is given in Table 2. As seen in Table 2, the prepared powder was composed mainly of MgO (more than 95%). The high content of MgO in the fabricated powder came from the burning of MgCO₃ at a high temperature, which thus converted it into MgO due to release of CO₂. The prepared powder had a BET specific surface area of 152 m²/g, with an average pore volume and size of 0.182 cm³/g and 4.8 nm, respectively, indicating the mesoporous characteristic of the powder. The SEM image indicated in Fig. 1 is used to visualize the surface morphology of the prepared MgO powder. The image shows porous, agglomerated and honey-combed nanocrystals. The XRD pattern of the prepared MgO powder is presented in Fig. 2 and indicates the periclase MgO crystalline particles in the powder.

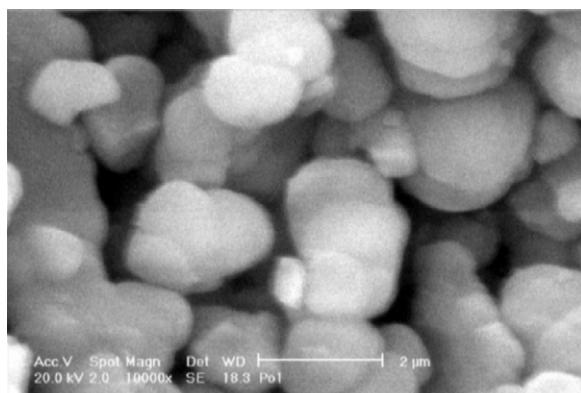


Fig. 1. The SEM image of the prepared MgO powder.

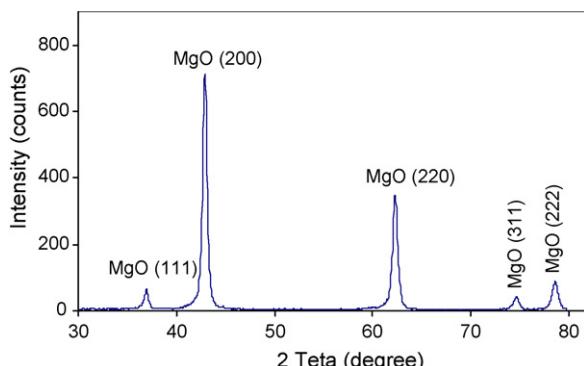


Fig. 2. The pattern of XRD of the prepared MgO powder.

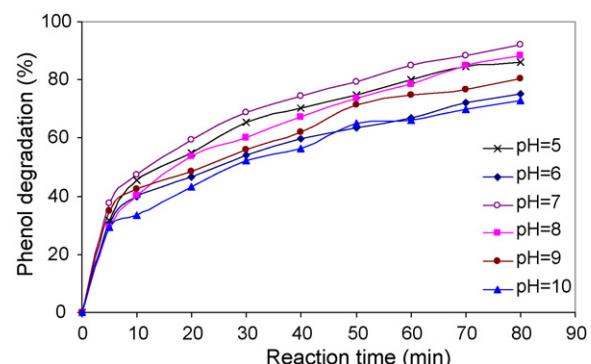


Fig. 3. The influence of pH on phenol degradation in the COP.

der. The average size of crystals as calculated from the Scherrer equation was found to be in the nano-range at 17.9 nm. Therefore, the prepared powder is mainly composed of MgO nanocrystal particles.

3.1.2. Influence of pH and synergy of MgO and ozone

Due to affecting the charge distribution on the catalysts' surfaces [48], as well as the pathways and kinetics of the ozone reactions [11], the pH of the solution plays a critical role in the overall performance of the COP. Therefore, a series of experiments were carried out under the conditions given in Table 1 to evaluate the catalytic ability of the prepared nanocrystal powder at different pHs in phenol degradation in saline wastewater. Fig. 3 depicts the time-course of phenol degradation at several solution pHs ranging from 5 to 10. As shown in Fig. 3, the degradation of phenol was highest at a pH of 7, where 92% of phenol was removed after an 80-min reaction time. For better observation of the pH influence, the kinetics of the reaction rate of phenol degradation was evaluated, and it was found that the pseudo-first-order reaction had the best fit with the experimental results. Table 3 contains the reaction constants of phenol degradation in the COP along with the determination coefficient (R^2) at different pHs, showing a high degree of fitness between the experimental data and the model. As seen in Table 3, the reaction rate constant was reduced from 0.021 to 0.013 l/min (corresponding to reduction of phenol degradation from 86% to 75%) when the pH was increased from 5 to 6; thereafter, it was increased up to the highest value of 0.027 l/min (phenol removal of 92%) when the pH was elevated to 7. After further increasing the solution pH to 10, the rate constant of the phenol degradation was progressively decreased by half and reached 0.013 l/min (phenol removal at pH 10 declined to 74%). In our previous study on catalytic ozonation of phenol in saline media with activated carbon as a catalyst [19], we found an optimum pH of 8, which is close to the pH found in the present work. Attainment of the maximum phenol degradation at neutral pH in the COP can be attributed to the complex interaction of O₃ and phenol molecules with the catalyst surface, which will be discussed further in the next section.

For a better illustration of the catalytic role of the prepared nano-powder compared to natural magnesite, the phenol degradation in COPs using MgO nanocrystals at the optimum pH was compared with that using magnesite/ozone, the single adsorption on the catalyst, as well as the single ozonation process (SOP) at similar conditions. The results are shown in Fig. 4. As can be

Table 3

Reaction rate constants of phenol degradation in the COP at various pHs.

Initial pH	5	6	7	8	9	10
k (l/min)	0.021	0.013	0.027	0.023	0.016	0.013
R^2	0.9916	0.9934	0.9936	0.9916	0.9906	0.9861

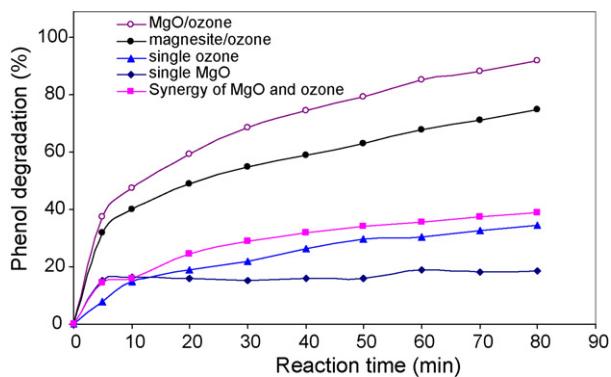


Fig. 4. Phenol removal by the COP, SOP, and adsorption onto catalyst particles, including the synergy of MgO and ozone.

observed in Fig. 4, around 16% of phenol was adsorbed onto the MgO nanocrystals during a short contact time of 5 min; thereafter, the adsorption percent remained almost unchanged up to an 80-min contact time. This reveals the low capacity and rapid adsorption of phenol on MgO nanocrystal powder and thus saturation of the catalyst. The degradation of phenol in SOPs increased from 8% for a 5-min reaction time to 35% after an 80-min reaction time, showing a pseudo-first-order degradation reaction ($R^2 > 0.97$) with a low rate constant of 0.004 l/min. It is worth noting that the pH of the solution in the SOPs descended from an initial value of 7 to around 3 after an 80-min reaction time. This is due to formation of some acidic intermediates such as oxalic, acetic and formic acids during the oxidation reaction [49]. According to Fig. 4, catalytic ozonation with natural magnesite achieved 75% phenol removal after an 80-min reaction time. In comparison, in the COP with MgO nanocrystals, as explained above, the oxidation of phenol linearly increased from 34% at a 5-min reaction to 92% after an 80-min reaction time, presenting a pseudo-first-order degradation constant of 0.027 l/min. This means that a 17% higher phenol degradation was obtained in the COP when using the calcined magnesite as a catalyst compared to use of original magnesite. Accordingly, the rest of the COP experiments were conducted with MgO nanocrystals as catalysts. The difference in catalytic ability of the calcined and original magnesite is due to the higher presence of MgO nanocrystals in the calcined magnesite (Table 2). It is seen, therefore, that adding the prepared MgO nanocrystals into the ozonation reactor in a small dose led to an acceleration of the phenol degradation, which was more than five times faster in COP than in SOP. Hence, this clearly qualitatively confirms a significant activity for the prepared nanocrystals used in the COPs. This is in accordance with He et al. [37], who found a higher degradation for phenol in aqueous solutions using ozonation with MgO than with brucite.

To quantify the contribution of the prepared MgO nanocrystals used in the COP in degrading phenol in saline wastewater, the synergistic influence achieved from adding the catalyst to the ozone reactor was calculated as [synergistic influence = phenol removed in COP – (sum of phenol removed in SOP and adsorbed onto the catalyst)], and the results are also plotted in Fig. 4. As evident in this figure, a significant synergistic influence (39% for an 80-min reaction time) was attained from combining the prepared MgO nanocrystals with ozone in phenol removal. This finding verifies the strong ability of the prepared MgO nanocrystals to catalyze the ozone reaction for degradation of phenol in saline wastewater.

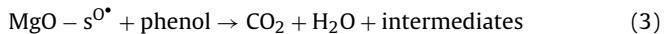
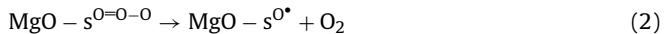
3.1.3. Mechanism of phenol degradation in COP

Following the attainment of an efficient removal of phenol from saline wastewater in the developed COP, an attempt was made to determine the possible mechanism involved in the phenol degradation. Two mechanisms are generally considered to work in the

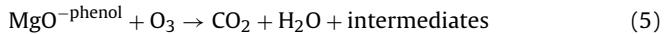
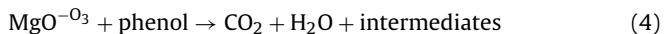
heterogeneous COPs of organic contaminants: direct reaction with ozone, and indirect reaction with the generated reactive radicals. Both mechanisms can occur in both the bulk solution and catalyst surfaces [30]. It is known that in COPs, the catalyst can accelerate the ozone decomposition and thereby formation of reactive radicals, mainly $\cdot\text{OH}$ [50]. To determine whether $\cdot\text{OH}$ is involved in the developed COP, the degradation of phenol was evaluated in the presence of tert-butanol, which is a known $\cdot\text{OH}$ scavenger [51], compared with the COP without the radical scavenger under the same experimental conditions (Table 1). The results of phenol removal in the COP both in the presence and absence of the tert-butanol are shown in Fig. 5. As seen in Fig. 5, the phenol degradation plots in the presence and absence of the radical scavenger were overlapped, implying no reduction of degradation rate upon addition of tert-butanol to the solution. By considering the point that tert-butanol causes the termination of the radical chain reactions due to its reaction with $\cdot\text{OH}$, generating the inert intermediates [50], the conclusion would be that the hydroxyl radical oxidation was not the dominant mechanism of phenol degradation in our COP under the selected conditions. This conclusion is in contrast to that of He et al. [37], who have reported the free hydroxyl radical mechanism for the degradation of phenol in the catalytic ozonation with MgO in a synthetic solution. The discrepancy can be related to the difference in salt content of the phenol solution under reaction in the two experiments. It is known that high concentrations of chloride ions in the solution can inhibit the generation of the $\cdot\text{OH}$ [35,52,53]. Therefore, mechanisms other than hydroxyl radical oxidation occurring in both the catalyst surfaces and the bulk solution have likely been involved in the process our experiment. The following mechanisms were therefore proposed for the phenol degradation in the COP:

At the surface of the catalyst:

- Radical type catalytic oxidation



- Direct oxidation with O_3 molecules



In the bulk solution:

- Direct oxidation with O_3 molecules

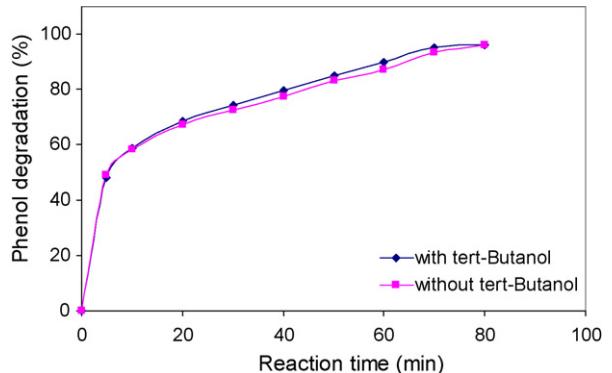


Fig. 5. Influence of tert-butanol as a $\cdot\text{OH}$ scavenger on phenol degradation in the COP.

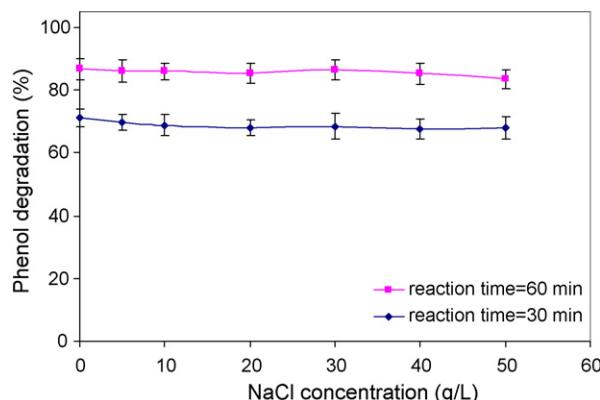


Fig. 6. Influence of catalyst dose on phenol degradation in the COP.

The suffix s in the MgO-s denotes the Lewis acid sites on the surface of MgO particles available for reacting with ozone.

According to Eq. (1), ozone molecules form hydrogen bonds with the hydroxyl groups on MgO nanocrystal surfaces; the bonded ozone then partly decomposes to atomic oxygen (Eq. (2)), thereby accelerating the catalytic ozonation [29,54] of the phenol (Eq. (3)). Undissociated ozone bonded with the MgO also directly oxidizes phenol coming into contact with it (Eq. (4)). As indicated in Fig. 4, part of the phenol is adsorbed onto the surface of the MgO particles that the O₃ can react with and degrades the adsorbed phenol molecules (Eq. (5)). Finally, O₃ and phenol molecules solubilized in the solution can directly react in the bulk solution, resulting in some degradation of phenol (Eq. (6)). All of the aforementioned mechanisms were involved in attaining the high removal of phenol in the COP. According to the synergistic influence observed between O₃ and MgO (Fig. 4), it can be deduced that the contribution of the reactions that occurred on the surface of the catalysts dominated.

3.1.4. Influence of salt concentration

Following the determination of the optimum operational pH for phenol degradation in the COP with the prepared MgO nanocrystals as the catalyst, a set of experiments (Table 1) was undertaken to investigate the influence of the salinity on the performance of the COP. The results are presented in Fig. 6 for reaction times of 30 and 60 min, showing a similar trend for phenol removal at both reaction times. As can be observed in Fig. 6, NaCl at high concentrations up to 50 g/L had no significant adverse influence on the designated COP in phenol degradation under the selected conditions. For instance, the average removal percentage of phenol was about 85% for a 60-min reaction time, regardless of the NaCl concentration. Independency of the performance of the developed COP in phenol degradation from the salinity medium can be explained by the mechanism prevailing in the process previously discussed, which was predominantly the direct oxidation by ozone rather than the indirect oxidation with •OH. We have recently reported phenol degradation in a saline medium using the COP with activated carbon as a catalyst, and the findings of the present work comply with our previous study [19]. The findings of the present work also comply with those of Bacardit et al. [55], who did not observe the adverse influence of chloride on the photo-Fenton process in the degradation of 4-chlorophenol. Nevertheless, several reports are available indicating that the chloride ion can inhibit the AOP performance in degrading contaminants [34,35,52,53], resulting in the reduction of the overall efficiency of the process. The inference from the above is that, contrary to the conventional AOPs, the developed COP in this study is not affected by the salinity of the solution during reactions, most likely due to the supporting degradation mechanism other than the free •OH oxidation. Therefore,

the prepared catalyst and the developed COP can be an efficient promising AOP alternative for degrading high concentration, toxic and inhibitory compounds such as phenol in saline liquid streams.

3.1.5. Influence of catalyst dose

The influence of dose of the prepared nanocrystal powder between wide ranges from 1 to 6 g/L was investigated on the degradation of phenol under conditions mentioned in Table 1. Fig. 7 presents the results of the 80-min reaction time-course. The results indicate that the phenol degradation percent in the COP increased from 30% to 88.3% with the increase of catalyst dose from 0 to 0.8 g, respectively, inferring that the dominant oxidation species were enhanced with the increase in catalyst dose [56]. In fact, as the surface of MgO is polar, it effectively adsorbs and thereby decomposes polar O₃ molecules [30]. Therefore, increase in the catalyst dose provides more surfaces available for the reaction with O₃, subsequently resulting in an increased oxidation rate [23,50]. These findings demonstrate a strong catalytic ability for the prepared nanocrystal powder for use along with the ozonation process in the degradation of toxic organic compounds in saline wastewater. After a further increase in the catalyst mass from 0.8 to 1.2 g, however, the phenol removal percentage remained almost unchanged. The concluding remark from Fig. 7 is that the COP with the prepared nanocrystal powder needs an optimal catalyst dose, value of which depends on the operational conditions as well as on the required degradation percent. In our previous studies [22,30], we found similar trends for catalytic ozonation with MgO nanocrystals, albeit under different experimental conditions and with organic compounds other than phenol, with the attainment of a different optimum dose. Another significant point in Fig. 7 is that the phenol degradation in the COP is higher in the first five minutes of the reaction, which can be related to the adsorption of the phenol onto the surface of the catalyst [57] (see Fig. 4).

3.1.6. Degree of degradation and COD removal of phenol in the COP under optimum experimental conditions

Upon determination of the optimum experimental conditions for which the COP achieved the highest degree of phenol degradation, the degree of degradation and COD removal of phenol in the COP was evaluated (see Table 1 for the experimental conditions). The mean of phenol degradation and its COD removal in the selected COP from duplicate experiments are indicated in Fig. 8. As can be observed in Fig. 8, the degradation of phenol in the COP under optimum experimental conditions increased almost linearly (first-order reaction with a constant of 0.022 l/min, R² = 0.981) with time and reached greater than 96% after an 80-min reaction time. The removal of COD in the COP had almost the same trend as phenol degradation, although with a lower rate (first-order reaction with a constant of 0.0123, R² = 0.981), reaching 70% after an

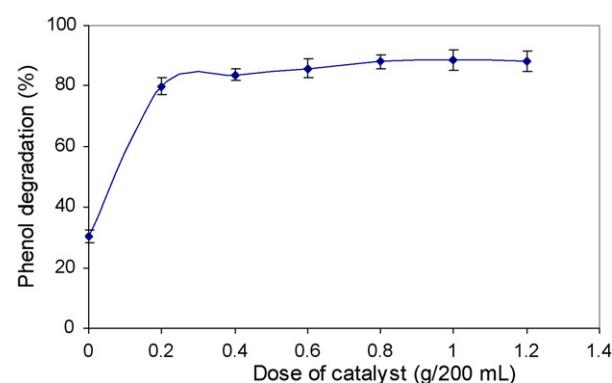


Fig. 7. Influence of NaCl concentration on degradation of phenol in the COP.

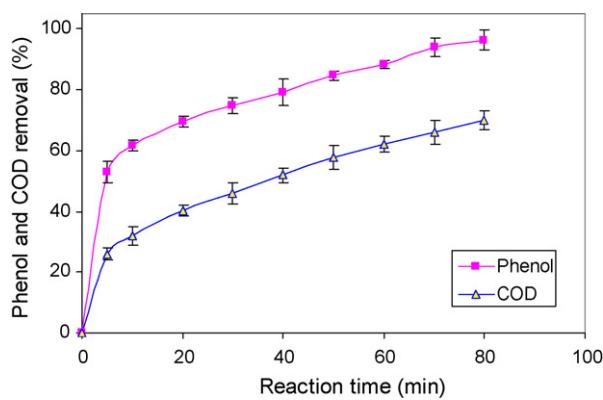


Fig. 8. Degradation and COD removal of phenol in the COP under optimum experimental conditions.

80-min reaction time. Therefore, the developed COP was able to achieve a significant degree of degradation and COD removal of the toxic compound of phenol in hyper-saline wastewater; whereas other AOPs, such as the Fenton, photo-Fenton [35], and photo-catalytic [58] processes, have been shown to be less efficient. We have also previously reported the considerable phenol degradation and COD removal of phenol in a COP with activated carbon as the catalyst [19]. However, the catalyst prepared in the present work indicated that a higher activity, leading to the requirement of a lower dose of catalyst for attaining a specific COD removal degree of phenol in saline wastewater. Furthermore, the production of the MgO nanocrystal powder from magnesite is simpler and thus less expensive than that of the activated carbon. Accordingly, it can be concluded that the produced nanocrystal powder is a promising catalyst for use in the ozonation process for degradation of the toxic organic compounds, particularly in saline media where other radical-based AOPs are almost less efficient due to the scavenging influence of chloride ions [53]. The difference between the value of phenol and COD removal at each reaction time equals the intermediates formed during the degradation of phenol, which were still measured as COD. Although the produced degradation intermediates were not specified, it will be indicated in the next section of the text that they were simple organic compounds and were efficiently biodegraded in a biological post-treatment process.

3.2. Biological post-treatment of the COP effluent

To exploit the advantages of a coupled COP and bioreactor for removal of high concentrations of phenol from hyper-saline wastewater, as well as to investigate the biodegradability of intermediates formed during degradation of phenol in the COP, the effluent from the investigated COP with a concentration of phenol below 100 mg/L was further treated in a lab-scale batch biological process using a suspended salt-acclimated biomass (see Table 1 for experimental conditions). Fig. 9 gives the average results of the duplicated biological experiments of raw and COP-pre-treated saline wastewaters. When using the raw feed (Fig. 9a), it took about 50 h for the COD to be reduced to below 100 mg/L (95% removal). Also, as seen in the inset of Fig. 9a, it took 20 h to decrease the phenol concentration to below 10 mg/L in the bioreactor when fed with the raw wastewater. In contrast, after pre-treating of the raw saline wastewater in the developed COP for a short reaction time of 80 min, the bioreactor could reduce the remaining effluent COD (around 800 mg/L) to 20 mg/L at a much shorter time of 10 h (Fig. 9b). The phenol remaining in the effluent of the COP was completely degraded in the bioreactor after 160 min of aeration (inset of Fig. 9b). These observations clearly depict that, contrary to phenol molecules, the oxidation intermediates formed during the

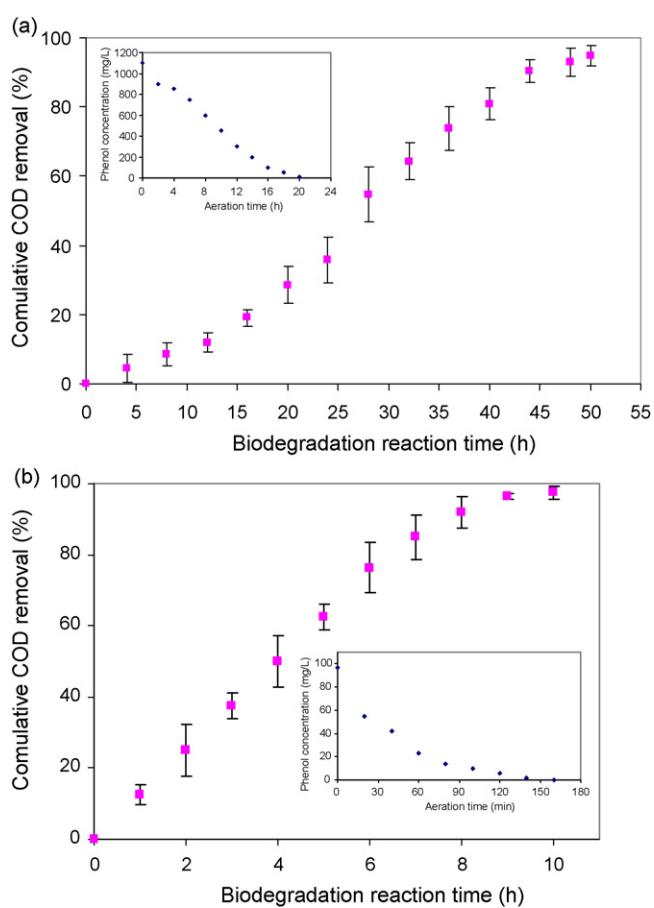


Fig. 9. Evolution of phenol and COD in the bioreactor for (a) raw phenol saline wastewater and (b) saline wastewater pre-treated in the COP.

catalytic ozonation of phenol are readily biodegradable. In other words, the COP could degrade the toxic phenol molecules into simple intermediates, thereby overcoming their inhibitory influence on the metabolism of microorganisms so that they could be rapidly biodegraded in the biological reactor [59]. Comparison of Fig. 9a and b, therefore, clearly reveals that the developed COP is a viable process for efficient pre-treating of hyper-saline wastewaters containing toxic and inhibitory compounds, the effluent of which is easily post-treated in a biological treatment in a much shorter treatment time. The overall finding is that, using the proposed integration, considerable savings would be gained for treating saline wastewater containing toxic compounds like phenol due to reduction of the time and thus size and cost of treatment, compared to the use of COPs or biological processes [60,61] as the stand-alone systems for treating such high strength waste streams.

4. Conclusions

The present work has explained first the preparation and characterization of a powder from natural magnesite. The findings of this part revealed that the prepared powder consisted mainly of mesoporous MgO nanocrystals of 17.9 nm in size, having $152 \text{ m}^2/\text{g}$ specific surface area. The prepared powder was then examined for its ability to catalyze ozonation for the degradation of phenol from saline wastewater, and it was found to have a higher catalytic capability compared with natural magnesite. A significant synergistic influence was observed when using MgO nanocrystals as catalysts in the zone reactor. Finally, the effluent from the treatment phenol in saline wastewater using the COP was efficiently post-treated in a biological process. It can therefore be concluded that the prepared

powder is a promising and attractive catalyst for use in catalytic ozonation of toxic compounds in saline media. Additionally, the integration of the developed COP with a biological process is an appropriate option for removal of recalcitrant compounds from saline wastewaters.

Acknowledgments

The authors would like to acknowledge the Tarbiat Modares University for technical and financial support. Authors would also like to thank Dr. N. Rashidnejad Omran for providing the magnesite ore and XRD analysis.

References

- [1] G. Busca, S. Berardinelli, C. Resini, L. Arrighi, J. Hazard. Mater. 160 (2008) 265–288.
- [2] J. Villaseñor, P. Reyes, G. Pecchi, Catal. Today 76 (2002) 121–131.
- [3] H.B. Senturk, D. Ozdes, A. Gundogdu, C. Duran, M. Soylak, J. Hazard. Mater. 172 (2009) 353–362.
- [4] ATSDR, Toxicological profile for phenol, 2008. Available at: <http://www.atsdr.cdc.gov/toxprofiles/tp115.html>. (accessed September 2008).
- [5] S.H. Lin, C.T. Shyu, M.C. Sun, Water Res. 32 (1998) 1059–1066.
- [6] N. Azbar, A. Bayram, A. Filibeli, A. Muezzinoglu, F. Sengul, A. Ozer, Crit. Rev. Environ. Sci. Technol. 34 (2004) 209–247.
- [7] F. Kargi, A.R. Dincer, Enzyme Microb. Technol. 19 (1996) 529–537.
- [8] O. Lefebvre, R. Moletta, Water Res. 40 (2006) 3671–3682.
- [9] A.G. Chakinala, D.H. Bremner, P.R. Gogate, K.-C. Namkung, A.E. Burgess, Appl. Catal. B 78 (2008) 11–18.
- [10] N.K. Kılıç, Int. Biodegr. Biodegr. 63 (2009) 778–781.
- [11] R.C. Martins, R.M. Quinta-Ferreira, Appl. Catal. B 90 (2009) 268–277.
- [12] X. Qu, J. Zheng, Y. Zhang, J. Colloid Interface Sci. 309 (2007) 429–434.
- [13] R. Thiruvenkatachari, T.O. Kwon, J.C. Jun, S. Balaji, M. Matheswaran, I.S. Moon, J. Hazard. Mater. 142 (2007) 308–314.
- [14] J.A. Melero, F. Martínez, J.A. Botas, R. Molina, M.I. Pariente, Water Res. 43 (2009) 4010–4018.
- [15] V.K. Gupta, Suhas, J. Environ. Manage. 90 (2009) 2313–2342.
- [16] I.A. Alaton, I.A. Balcioglu, D.W. Bahnemann, Water Res. 36 (2002) 1143–1154.
- [17] R.F. de Sena, J.L. Tambosi, A.K. Genena, R.F.P.M. Moreira, H.Fr. Schröder, H.J. José, Chem. Eng. J. 152 (2009) 151–157.
- [18] H. Jung, H. Park, J. Kim, J.-H. Lee, H.-G. Hur, N.V. Myung, H. Choi, Environ. Sci. Technol. 41 (2007) 4741–4747.
- [19] G. Moussavi, A. Khavanin, R. Alizadeh, J. Hazard. Mater. 171 (2009) 175–181.
- [20] L.F. Liotta, M. Gruttaduria, G. Di Carlo, G. Perrini, V. Librando, J. Hazard. Mater. 162 (2009) 588–606.
- [21] L. Zhao, J. Ma, Z. Sun, H. Liu, J. Hazard. Mater. 167 (2009) 1119–1125.
- [22] G. Moussavi, M. Mahmoudi, Chem. Eng. J. 152 (2009) 1–7.
- [23] Y.-F. Zeng, Z.-L. Liu, Z.-Z. Qin, J. Hazard. Mater. 162 (2009) 682–687.
- [24] F. Qi, B. Xu, Z. Chen, J. Ma, D. Sun, L. Zhang, Sep. Purif. Technol. 66 (2009) 405–410.
- [25] D. Li, J. Qu, J. Environ. Sci. 21 (2009) 713–719.
- [26] Y. Dong, H. Yang, K. He, S. Song, A. Zhang, Appl. Catal. B 85 (2009) 155–161.
- [27] P.C.C. Faria, D.C.M. Monteiro, J.J.M. Órfão, M.F.R. Pereira, Chemosphere 74 (2009) 818–824.
- [28] R. Rosal, M.S. Gonzalo, A. Rodríguez, E. García-Calvo, J. Hazard. Mater. 169 (2009) 411–418.
- [29] H.C. Wang, S.H. Chang, P.C. Hung, J.F. Hwang, M.B. Chang, J. Hazard. Mater. 164 (2009) 1452–1459.
- [30] G. Moussavi, A. Yazdanbakhsh, M. Heidarizad, J. Hazard. Mater. 171 (2009) 907–913.
- [31] M.A. Aramendía, V. Borau, C. Jiménez, J.M. Marinas, J.R. Ruiz, F.J. Urbano, Appl. Catal. A 244 (2003) 207–215.
- [32] I.V. Mishakov, A.F. Bedilo, R.M. Richards, V.V. Chesnokov, A.M. Volodin, V.I. Zaikovskii, R.A. Buyanov, K.J. Klabunde, J. Catal. 206 (2002) 40–48.
- [33] R. Richards, R.S. Mulukutla, I. Mishakov, V. Chesnokov, A. Volodin, V. Zaikovskii, N. Sun, K.J. Klabunde, Scripta Mater. 44 (2001) 1663–1666.
- [34] E.M. Siedlecka, P. Stepnowski, Sep. Purif. Technol. 52 (2006) 317–324.
- [35] R. Maciel, G.L. Sant'Anna Jr., M. Dezotti, Chemosphere 57 (2004) 711–719.
- [36] E.B. Azevedo, F.R.A. Neto, M. Dezotti, J. Hazard. Mater. 128 (2006) 182–191.
- [37] K. He, Y.M. Dong, Z. Li, L. Yin, A.M. Zhang, Y.C. Zheng, J. Hazard. Mater. 159 (2008) 587–592.
- [38] D. Mantzavinos, E. Psillakis, J. Chem. Technol. Biotechnol. 79 (2004) 431–454.
- [39] D.W. Tedder, F.G. Pohland, Emerging Technologies in Hazardous Waste Management III, American Chemical Society, Washington, DC, 1993.
- [40] P.R. Gogate, A.B. Pandit, Adv. Environ. Res. 8 (2004) 553–597.
- [41] A. Marco, S. Esplugas, G. Saum, Water Sci. Technol. 35 (1997) 321–327.
- [42] M. Pera-Titus, V. García-Molina, M.A. Baños, J. Giménez, S. Esplugas, Appl. Catal. B 47 (2004) 219–256.
- [43] V.S.S. Birchall, S.D.F. Rocha, V.S.T. Ciminelli, Miner. Eng. 13 (2000) 1629–1633.
- [44] S. Altenor, B. Carene, E. Emmanuel, J. Lambert, J.-Jacques Ehrhardt, S. Gaspard, J. Hazard. Mater. 165 (2009) 1029–1039.
- [45] B.D. Cullity, S.R. Stock, Elements of X-Ray Diffraction, 3rd ed., Prentice-Hall, New Jersey, 2001.
- [46] G. Moussavi, M. Mahmoudi, B. Barikbin, Water Res. 43 (2009) 1295–1302.
- [47] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, 21st ed., APHA, AWWA, WEF, Washington, DC, 2005.
- [48] F.J. Beltrán, P. Pocostales, P.M. Álvarez, F. López-Piñeiro, Appl. Catal. B 92 (2009) 262–270.
- [49] A. Santos, P. Yustos, T. Cordero, S. Gomis, S. Rodríguez, F. García-Ochoa, Catal. Today 102 (2005) 213–218.
- [50] L. Zhao, J. Ma, Z.-z. Sun, X.-d. Zhai, Appl. Catal. B 83 (2008) 256–264.
- [51] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, Catal. Commun. 9 (2008) 2121–2126.
- [52] E. Lipczynska-Kochany, G. Sprah, S. Harms, Chemosphere 30 (1995) 9–20.
- [53] M.C. Lu, J.N. Chen, C.P. Chang, Chemosphere 35 (1997) 2285–2293.
- [54] T. Zhang, C. Li, J. Ma, H. Tian, Z. Qiang, Appl. Catal. B 82 (2008) 131–137.
- [55] J. Bacardit, J. Sttzner, E. Chamorro, S. Esplugas, Ind. Eng. Chem. Res. 46 (2007) 7615–7619.
- [56] Z.Z. Xu, Z.L. Chen, C. Joll, Y. Ben, J.M. Shen, H. Tao, Catal. Commun. 10 (2009) 1221–1225.
- [57] S.M. Avramescu, C. Bradu, I. Udrea, N. Mihalache, F. Ruta, Catal. Commun. 9 (2008) 2386–2391.
- [58] E.B. Azevedo, F.R. de Aquino Neto, M. Dezotti, Appl. Catal. B 54 (2004) 165–173.
- [59] K.V. Shetty, R. Ramanjaneyulu, G. Srinikethan, J. Hazard. Mater. 149 (2007) 452–459.
- [60] C.R. Woolard, R.L. Irvine, Water Environ. Res. 66 (1994) 230–235.
- [61] C.R. Woolard, R.L. Irvine, Water Res. 29 (1995) 1159–1168.